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COLORADO STATE UNIV FORT COLLINS DEPT OF CHEMISTRY
ELECTROCHEMISTRY OF SOLUTES IN CHLOROALUMINATE MELTS AND THE DE--ETC(U)
1979 R A OSTERYOUNG , J G OSTERYOUNG AFOSR-76-2978

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Research carried out under this grant had, as its primary goal, the investigation of molten haloaluminates as solvent systems for the study of electrochemical reactions. The particular interest has been in the fact that systems, such as the molten tetrachloroaluminates, show significant acid-base dependent behavior which is reflected in solute electrochemistry.			
In the NaCl:AlCl ₃ system (sodium tetrachloroaluminate), the acid-base chemistry of oxides and chalcogenides was investigated. The electrochemistry of Mo, Se and Te			

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was investigated; Mo was studies in the basic melt (excess NaCl) while Se and Te were investigated as a function of melt acidity and a variety of acidity dependent electrochemical reactions were uncovered. The electrochemistry of Ni(II) was also investigated, and it was found that NiCl_2 was insoluble in the neutral and basic melt. At 175°C the melt becomes saturated with NaCl at about 1% excess. Although not subject to detailed investigation, it was found that oxygen reduction in this melt could be catalyzed by the presence of metal cations. Such as Cu(I) and Mo(V).

A new "room temperature" molten salt, N-Butylpyridinium chloride (BuPyCl)-aluminum chloride, was discovered. The 1:1 mole ratio mixture of $\text{BuPyCl}:\text{AlCl}_3$ is liquid at 27°C , and the mole ratio may be varied from 1:0.6 to 1:2 at essentially room temperature, thus permitting significant variation in acidity. Raman spectroscopic studies were carried out and the dominant solvent equilibrium, $2 \text{ AlCl}_4^- = \text{Al}_2\text{Cl}_7^- + \text{Cl}^-$, was determined potentiometrically as $\leq 3.8 \times 10^{-13}$ on the mole fraction scale, the limitation being imposed because the BuPy^+ species is reduced by an Al indicator electrode in the basic melt, thus rendering precise determination of this constant difficult. This melt is miscible with benzene and other organic solvents and nmr studies indicated that the benzene undergoes no specific interaction with the melt, serving as a simple diluent. Determination of the dominant equilibrium referred to above in a 50-50 volume precent mixture of melt plus benzene gave a value for the equilibrium constant essentially identical to that for the pure melt. This again indicates the absence of any specific interaction of the melt with the benzene. A number of physical properties - conductivity, and viscosity, in particular - are improved upon addition of benzene.

The Raman, potentiometry and other physical studies indicated that the 1:1 melt is essentially $\text{BuPy}^+ + \text{AlCl}_4^-$, while the 2:1 $\text{AlCl}_3:\text{BuPyCl}$ system can be regarded as $\text{BuPy}^+ + \text{Al}_2\text{Cl}_7^-$. The equilibrium, $\text{AlCl}_3 + \text{AlCl}_4^- \rightleftharpoons \text{Al}_2\text{Cl}_7^-$ lies much further to the right than in the corresponding alkali halide-aluminum halide systems, even when the temperature difference of the systems is taken into account.

The electrochemistry of a number of aromatic polynuclear hydrocarbons was studied across the acidity range. All were shown to undergo a one-electron oxidation to the radical cation that was independent of melt acidity and, compared to ferrocene, oxidized at the same relative potential as in acetonitrile. At high acidity, certain of the hydrocarbons appeared to participate in acid-base chemistry with the melt, and it was postulated that an aluminum chloride analog of a carbonium ion was formed. Some of the more easily oxidized hydrocarbons were spontaneously oxidized by the most acid melt mixture.

In related work, the electrochemistry of a number of metal carbonyls was investigated in another room temperature melt, a 2:1 mixture of aluminum chloride and ethylpyridinium bromide. Attempts to study the electrochemistry of iron diimine complexes failed, since it was found that the Fe(II) complexes underwent photochemical conversion to the Fe(III) complexes.

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This is the Final Report on AFOSR-[redacted], "Electrochemistry of Solutes in Chloroaluminate Melts and the Development of Related Electrochemical Methodology.

The research carried out under this grant was intended to investigate molten haloaluminate melts as solvents for chemical reactions, with particular emphasis on the electrochemical behavior of solutes in these systems. To do this, a variety of electrochemical and non-electrochemical work is required in order to obtain a firmer understanding of the solvent system characteristics and, in particular, the acid-base dependent chemistry in the system. As of February, 1979, a new task involving the development of electrochemical methodology specifically aimed at aiding the performance of this work was added.

The grant period was from 1 April, 1976 thru 30 June, 1979. Total funds for the period amounted to \$148,000. In the initial stages of this grant only one of us (RAO) was a principal investigator. However, an additional co-principal investigator was added as of February, 1979. During the period of this grant one of us (RAO) spent a year on leave in Washington at the Air Force Office of Scientific Research. During that period Professor Elliott Bernstein served as Principal Investigator. The project was initially funded for \$50,000 and an additional \$80,000 was funded 1 March, 1977. The initial funding was intended for 6 months, but a no cost extension was requested. In view of the Principal Investigators Washington sojourn, another no-cost extension was requested. A renewal proposal for \$100,000 effective 1 February, 1979, was prepared but, in view of the fact that the co-principal investigators were leaving Colorado State University for the State University of New York at Buffalo, this was decreased to \$18,000 with a termination date of 30 June, 1979. Hence, the 3.25 year period of this grant was funded for approximately 1.6 to 1.7 years of funding, as requested in the initial proposal submitted in June, 1975.

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I. Work in Sodium Tetrachloroaluminate

In the interests of brevity, material which has been published will be covered by inclusion of abstract, with appropriate references.

Appendix I includes a cumulative list of publications on AFOSR funding, or related funding; work performed on prior AFOSR grants and previously included in past Final Reports, but which was published since April, 1976, includes references 14, 15, 16 and 17.

Studies of Molybdenum chemistry in the basic sodium tetrachloroaluminate melt were completed and published (18). An abstract of the published paper follows:

"A number of molybdenum chlorides and oxychlorides have been investigated in the sodium tetrachloroaluminate melt. The three- and five-oxidation states were stable in the melt, but the six-oxidation state, added as MoO_3 , MoO_2Cl_2 , and MoOCl_4 , oxidized the melt and was itself reduced to Mo(V). The behavior of this Mo(V) was indistinguishable from that of Mo(V) added directly to the melt as the pentachloride. Mechanisms have been proposed to rationalize the electrochemical oxidation of Mo(III) and reduction of Mo(V), although in the latter case layer formation on the electrode surface prevented a definitive characterization. A disproportionation mechanism is believed to be operative in the oxidation of Mo(III), and by cyclic voltammetry and rotating ring-disk techniques it has been possible to detect an intermediate Mo(IV) species."

Continued interest in the acid-base dependent chemistry of solutes in these melts lead to a further investigation of the acidity dependence of oxides and chalcogenide ions in the sodium tetrachloroaluminate melt.

This work has been published in Inorganic Chemistry (19). An abstract

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of that material follows:

"The acid-base chemistry of oxide, sulfide, selenide, and telluride ions in sodium tetrachloroaluminate melts at 175°C has been investigated. These ions were found to be trichloro bases in acidic melts, the equilibrium with the solvent being $3\text{Al}_2\text{Cl}_7^- + \text{X}^{2-} \rightleftharpoons \text{AlXCl}_2^- + 3\text{AlCl}_4^-$. Within the precision of the present results the relative strengths of the tribases appear to be in the order $\text{Te}^{2-} < \text{Se}^{2-} < \text{S}^{2-} < \text{O}^{2-}$."

A desire to attempt to determine oxide ions in the melt lead to our attempting to repeat work published by Tremillion and coworkers (B. Tremillion, A. Bermond and R. Molina, J. Electroanal. Chem., 74, 53 (1976)). We were unable to repeat this work and a detailed study was made of the behavior of nickel in the sodium tetrachloroaluminate melt. This work was published in the Journal of the American Chemical Society (24) and an abstract follows:

"The electrochemical behavior of Ni(II) has been investigated in chloroaluminate melts between 175 and 210°C. Ni(II) is completely soluble in acidic mixtures where the pCl is higher than 5.5 (mol kg^{-1} scale). A well-defined and behaved reduction wave is observed at 1.2V vs. an Al reference in a NaCl-saturated reference compartment. When the pCl is decreased, precipitation of NiCl_2 occurs, the result which has been confirmed from electrochemical and x-ray diffraction experiments. A solubility product of $10^{-12.9}$ (mol kg^{-1})³ was found. This result is also in disagreement with the precipitation of NiO which has been recently proposed in the literature. As a direct consequence, the acid-base behavior of oxide ions in chloroaluminate has been reinvestigated. Precise titrations of the basic strength of oxide ions have been performed in narrow pCl ranges. An equilibrium constant of 1.6×10^{-2} mol

kg^{-1} was found for the general reaction $\text{AlOCl}_2^- \rightleftharpoons \text{AlOCl} + \text{Cl}^-$, two orders of magnitude higher than the previously reported value."

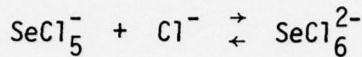
It is at least of passing interest to note that a private conversation with Professor Tremillion at the International Society of Electrochemistry meeting in Trondheim, Norway in August of 1979 resulted in his stating that they had been unable to repeat their own published work.

Work on the behavior of the chalcogenides in the melt was continued, in keeping with our prior work on sulfur (16).

Studies on the behavior of selenium and tellurium in the sodium tetrachloroaluminate melts were carried out and published in the Journal of the Electrochemical Society (23,27). Abstracts of those papers follows:

"The electrochemistry of selenium and various selenium compounds in $\text{AlCl}_3:\text{NaCl}$ melts has been investigated by a variety of techniques including pulse and cyclic voltammetry, coulometry, and the rotating-disk electrode. It was found that selenium can be reduced, in both acid and basic melts, by a single two-electron step to selenide which exists in the melt as either AlSeCl or AlSeCl_2^- (or their analogous solvated species $\text{Al}_2\text{SeCl}_5^-$ and $\text{Al}_2\text{SeCl}_6^{2-}$) depending upon the acidity. The mechanism for the oxidation of selenium to Se(IV) was found to be dependent upon the melt acidity. In basic melts, selenium was first oxidized by a two-electron step to an Se(II) species and then by a further two-electron step to Se(IV). In acid melts the oxidation was a single quasireversible four-electron step. The reduction of Se(IV) to selenium was a single four-electron step at all melt acidities. The kinetics of these oxidation and reduction processes were investigated extensively. From studying SeCl_4 solutions, it was found that there were two Se(IV) species

in the melt, SeCl_6^{2-} and SeCl_5^- , linked by the acidity-dependent equilibrium



for which the equilibrium constant was calculated to be $6.0 \pm 1.0 \times 10^3$ on the mole fraction scale."

"The electrochemistry of Te(IV) in NaCl:AlCl_3 melts has been investigated by a variety of techniques including cyclic and pulse voltammetry, potentiometry, controlled potential coulometry, and the use of the rotating-disk electrode. It was found that in the most basic melts at temperatures above 250°C , Te(IV) was initially reduced by a two-electron step to a soluble Te(II) species which could then be reduced further to elemental tellurium. At lower temperatures and in more acidic melts, Te(IV), which is present in the melt as the chlorocomplex ion TeCl_3^+ , is reduced directly to Te which undergoes a complexation reaction with Te(IV) to form Te_4^{2+} . This complexation reaction and the oxidation of Te_4^{2+} have both been extensively investigated and a mechanism for the complexation reaction involving a Te(II) intermediate is proposed."

It was also discovered that oxygen, which is unreactive at an electrode in the melt, could be catalytically reduced by the presence of traces of metallic ions, such as Cu(I) or Mo(V), in the melt. It is hoped to utilize this discovery in future research activities in this solvent.

A review article dealing with aspects of our prior work and that of others has been co-authored with Professor Gleb Mamantov, also an AFOSR grantee, and published in a book arising from presentations at an American Chemical Society symposium (25).

II. Work in "Room Temperature" Molten Salts

Many years ago, under AFOSR 71-1995, we initiated some electrochemical studies of the behavior of organic solutes in the sodium tetrachloroaluminate melts (4,6,9). This work was then split off, and, in collaboration with Professor Larry Miller, then of Colorado State University, a research proposal was submitted to, and supported by, the Army Research Office. Partial support from the American Chemical Society-Petroleum Research Fund was also obtained. Several publications are attributed to this support as well as to AFOSR support and aid (8,12,14). However, it was clear that the high temperature (175°C) required for the sodium tetrachloroaluminate melt precluded extensive utilization as a solute for organic reactions, though very interesting properties, such as the surprising stability of radical cations, was noted.

We then discovered that a system of ethylpyridinium bromide-aluminum chloride (1:2 mole ratio) had been studied briefly in the early 50's (F.H. Hurley and T.P. Wier, J. Electrochem. Soc., 98, 203 (1951)) and we utilized this system as a "room temperature" molten salt, since it was liquid at essentially room temperature (11,15).

Under the present support, the behavior of a number of metal carbonyls in a mixture of this room temperature melt with benzene, with which it is miscible was studied and published in the Journal of Organometallic Chemistry (21). An abstract of that work follows:

"The electrochemical oxidation of six metal carbonyls was studied in a mixture of the high Lewis acid, room temperature molten salt, composed of aluminum chloride and ethylpyridinium bromide (2:1 molar ratio) and benzene (50% v/v). Chromium hexacarbonyl was found to be reversibly oxidized to the seventeen electron cation $\text{Cr}(\text{CO})_6^+$, isoelectronic with vanadium hexacarbonyl. Some stability was also found for the

corresponding 17 electron cation of iron pentacarbonyl. The other carbonyl compounds studied $\text{Mo}(\text{CO})_6$, $\text{W}(\text{CO})_6$, $\text{Re}_2(\text{CO})_{10}$, and $\text{Mn}_2(\text{CO})_{10}$ exhibit electrochemical behavior characteristic of chemical and electrochemical reactions following the electron transfer reaction. Based on the large dependence of the oxidation potentials on the nature of the central metal atom in this solvent, it is proposed that the metal carbonyls interact with electron deficient species in the melt, decreasing the α donor ability of the ligand, but increasing its π acceptor capabilities."

One of our colleagues at that time had an interest in iron diimine complexes, and aside was made to study a bit of their behavior in aqueous acid solution. This work was published in Inorganic Chemistry (20). An abstract of that work follows:

"The electrochemical oxidation of tris(glyoxal bis(methylimine)-iron(II), $\text{Fe}(\text{GMI})_3^{2+}$, has been investigated using cyclic voltammetry and rotating-disk studies in 0.5 M H_2SO_4 . The main reaction product is an iron(III) complex in which one of the GMI ligands is oxidized to $\text{H}_3\text{CN}=\text{C}(\text{OH})-\text{CH}=\text{NCH}_3$, thus consuming 3F/mol of $\text{Fe}(\text{GMI})_3^{2+}$. A reaction mechanism consisting of electrochemical oxidation of the Fe(II) to an Fe(III) complex followed by a rate-determining first-order chemical reaction is proposed. In this chemical reaction, the Fe(III) complex is intramolecularly reduced to the Fe(II) state, with concomitant oxidation of the ligand; the radical-ligand complex is then further electrochemically oxidized very rapidly. This proposed ECE mechanism is compatible with the experimental results. The rate for the intramolecular reduction of the ferric complex is $22 \pm 2 \text{ s}^{-1}$. This value is applied to estimate a second-order rate constant of $10^9\text{-}10^{10} \text{ M}^{-1} \text{ s}^{-1}$ for the chemical oxidation of $\text{Fe}(\text{GMI})_3^{2+}$ in this acid concentration."

When efforts to study these complexes in the room temperature, acid molten salt were made, however, it was found that the complexes were photosensitive, and a brief study of this phenomenon was made and published as a Communication in the Journal of the American Chemical Society (22). Briefly, it was found that most of the Fe(II) complexes of the iron diimines studied were converted into their Fe(III) complexes on irradiation with low intensity visible light. It was concluded that the reaction, which resulted in the oxidation of the complex involved the ethylpyridinium cation as an electron acceptor, which could then dimerize. This publication must, however, be considered as somewhat non-definitive, but further work was considered beyond the scope of our normal research interests.

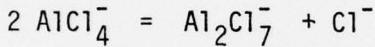
The ethylpyridinium bromide-aluminum chloride (1:2 mole ratio system) possessed significant limitations, however. It is only about the 1:1 mole ratio of aluminum chloride to organic halide (or inorganic halide) that the acidity of the system may be significantly varied (3). Thus, we continued to seek a low melting system where the mole ratio could be varied about the 1:1 point.

In the spring of 1977, this hope was realized. We found that the system N-butylpyridinium chloride-aluminum chloride was liquid at 27°C and that the mole ratio of N-butylpyridinium chloride to aluminum chloride could be varied from 1:0.6 to 1:2, i.e., it could be made very basic with excess butylpyridinium chloride and quite acid in the 1:2 mole ratio melt. A number of publications have resulted from this finding.

First, Raman spectral studies were performed and the results have been published in Inorganic Chemistry (26). The abstract follows:

"The Raman spectra of AlCl_3 -1-butylpyridinium chloride liquids at ambient temperatures have been recorded for the 0.75:1.0 to 2.0:1.0 molar composition range, respectively. Four absorption bands each for AlCl_4^- and for Al_2Cl_7^- ionic species were assigned on the basis of higher temperature vibrational spectral results of AlCl_3 -alkali metal chloride systems. The association equilibrium constant for Al_2Cl_7^- ion formation, $2\text{AlCl}_4^- + \text{Al}_2\text{Cl}_6 \rightleftharpoons 2\text{Al}_2\text{Cl}_7^-$ is significantly larger than that for the AlCl_3 -MCl melts, where M represents an alkali metal cation."

Following that, it became necessary to determine the equilibrium constant for the dominant melt equilibria,



and this was done. The results have been published, also in Inorganic Chemistry (29). The abstract follows:

"The solvent acid-base properties of AlCl_3 :1-butylpyridinium chloride melts from 2.2:1.0 to 0.6:1.0 molar ratios have been investigated by potentiometry. An equilibrium constant, K_3 , for the dissociation reaction $2\text{AlCl}_4^- \rightleftharpoons \text{Al}_2\text{Cl}_7^- + \text{Cl}^-$ was determined to be $< 3.8 \times 10^{-13}$ at 30°C. The 1-butylpyridinium cation is spontaneously reduced by elemental aluminum in the basic composition range."

Several years ago we had initiated certain physical property studies on the ethylpyridinium halide-aluminum halide "room temperature" melt. This was later expanded to include work on the butylpyridinium chloride-aluminum chloride system, and also included some nuclear magnetic resonance studies. While bringing this work to fruition proved difficult, it was finally done. Of primary importance is the fact that these room temperature melts are miscible with benzene, and other organic solvents, although there is no evidence of complex formation between the aluminum

chloride and the benzene. This work has been published in the Journal of the American Chemical Society (30). An abstract follows:

"A molten salt system AlCl_3 -n-butylpyridinium chloride has been developed which is molten at 40°C over a wide composition range (0.75:1 to 2:1 mole ratio AlCl_3 -n-butylpyridinium chloride) and the electrochemical and spectroscopic behavior of a number of aromatic hydrocarbons has been investigated in this medium. All the hydrocarbons studied were shown to undergo a one-electron oxidation to the cation radical at a potential that is independent of the melt composition and similar to the value in acetonitrile. The oxidation potential in the melt was found to vary fairly linearly with the value of the first ionization potential of the hydrocarbon and the cation radicals formed were observed to have a significantly greater stability in this molten salt medium than in acetonitrile. Spectroscopic studies showed that the hydrocarbons participate in an acid-base type equilibrium with the acid species in the melt, Al_2Cl_7^- , to yield complexes whose spectra were generally very similar to those of the carbonium ions of the parent hydrocarbons. The 1:1 melt was shown to be capable of oxidizing those hydrocarbons more readily oxidized than hexamethylbenzene to their radical cations. This oxidation ceased when the melt acidity was lowered."

Since it was felt that the mixtures of the melt with benzene were important, the behavior of aluminum in the melt and the melt-benzene mixture was investigated. This work is in press in the Journal of Electrochemical Society (31). Of primary importance is the fact that the dominant equilibrium in the melt - benzene mixture is essentially the same as that in the pure melt, again substantiating the fact that

the benzene serves as a simple diluent. An abstract of that paper follows:

"The aluminum deposition and stripping processes at tungsten, platinum and glassy carbon electrodes in the low temperature molten salt system, n-butylpyridinium chloride: aluminum chloride and the 50 vol% mixture of this molten salt with benzene has been investigated. At all three electrodes, and in both solvent systems, the deposition reaction in slightly acidic melts, the reduction of Al_2Cl_7^- ions, was found to involve a nucleation process while at the tungsten and platinum electrodes under-potential deposition was also observed. Reduction of the n-butylpyridinium cation was found to occur at -1.1V vs. Al(2:1 melt) which is positive of the reduction potential of AlCl_4^- ions and therefore aluminum deposition in basic melts was not observable. Studies of the stripping of aluminum from inert substrates showed that aluminum is very slowly corroded in acidic melts, and melt-benzene mixtures, by traces of oxidizing impurities while in basic systems aluminum reduces the butylpyridinium cation. Potentiometric titration of the 50 vol% melt-benzene mixture showed that the acid-base properties of this system are defined, as in the pure melt, by the equilibrium



with an equilibrium constant of 2.2×10^{-13} at 30°C .

Finally, two review articles dealing predominantly with the room temperature molten salt work have been prepared for publication (32,33).

It should be mentioned that the discovery of these 1:1 melts was quickly transmitted to personnel at the Frank J. Seiler Research Laboratory at the Air Force Academy in Colorado Springs. They have investigated the properties of several related systems (R.A. Carpio, L.A. King,

R.E. Lindstrom, J.C. Nardi and C.L. Hussey, J. Electrochem. Soc., in press) and have studied the behavior of the Cu(II)-Cu(I) system in a very acid (2:1) melt of aluminum chloride - methylpyridinium chloride (C.L. Hussey, L.A. King and R.A. Carpio, J. Electrochem. Soc., 126, 1029 (1979) and the Fe(III)-Fe(II) system in the 2:1 aluminum chloride-N-butylypyridinium chloride melt (C.L. Hussey and L.A. King, J. Electrochem. Soc., in press).

Although not related directly to this grant work, a recent development is worth noting. It has been found that the room temperature melts may be useful solvents for carrying out photochemical conversion, via a photoelectrochemical device. During the Spring of 1979 some preliminary experiments, in collaboration with Dr. Arthur Nozik of the Solar Energy Research Institute Golden, Colorado were carried out and were reported. (R.J. Gale, A.J. Nozik, and R.A. Osteryoung, "Electrochemical Characterization of the Semiconductor TiO₂-Room Temperature Molten Salt Interface", Rocky Mountain Regional Electrochemical Society Meeting, Ft. Collins, Colorado, June, 1979). While the results were of a preliminary nature, they did indicate that the electrodes were stable in the melts and that a variation in flat-band potential with melt acidity could be noted. Further work in this area, in collaboration with Dr. Nozik, will be carried out. A number of other workers now appear to have become intrigued with this possibility, and as a result of our work on these melts, activity is going on at Colorado State University (in Electrical Engineering and Chemistry,) at Gould, Inc., Rolling Meadows, Illinois, at the Solar Energy Research Institute, and at the Massachusetts Institute of Technology, where Professor Mark Wrighton is preparing to

initiate some work in photoelectrochemistry in these solvents. It is therefore possible that our work in, and discovery of, these unique low temperature molten salt systems could be of considerable technological importance.

III. Interaction with Air Force and other DOD Laboratories

During the course of this work continual contact has been maintained with personnel at the Seiler Laboratory, particularly Lt. Col. Lowell King and co-workers. Several meetings were held, both at Colorado Springs and in Fort Collins. As mentioned above, communication regarding the discovery of the low temperature melts was quickly made to Seiler Laboratory; some effort was made in Fort Collins - with no success, sad to say - to run Raman on some of the other alkylpyridinium halide melts they prepared. The most recent meeting was held at Seiler on May 2, 1979, prior to leaving Colorado State University. It is hoped that continued contact with Seiler will prove possible even though we are now physically further away.

Presentation on work under this grant was made at the Analytical Contractors Meeting in Dayton in June, 1979. As a result of that presentation, samples of the butylpyridinium chloride material were sent to Dr. David Margerum at Hughes Research Research Laboratory in California; he was interested in assessing it as an additive in some of his liquid crystal work.

It should be added that work to perform spectroscopic studies in non-aqueous systems, including these molten salts, is funded by the Office of Naval Research. Some of the publications listed render

credit, when applicable, to both ONR and AFOSR. Presentations on portions of this work have been made at several ONR contractors' meetings.

IV. Grant Personnel

Individuals associated with this grant activity for any prolonged period of time are listed below. All were at the post-doctoral level.

Dr. Graham Cheek
Dr. Thomas Santa Cruz
Dr. Robert Gale
Dr. Bernard Gilbert
Dr. David Koran
Dr. Hogne Linga
Dr. Jeffrey Phillips
Dr. James Robinson

APPENDIX I

Publications--Grant Related Activity - since AFOSR support initiated.

AFOSR-71-1995; 1 Jan. 1971 - 28 Feb. 1975; Final Report 30 June 1975.

1. Janet Osteryoung and R.A. Osteryoung, "The Advantage of Charge Measurements for Determining Kinetic Parameters," *Electrochimica Acta*, 16, 525 (1971).
2. R.A. Osteryoung, "Introduction to the On-Line Use of Computers in Electrochemistry," Vol. II, "Application of Computers to Chemical Instrumentation," Ed. by Mattson, Mark and MacDonald, Marcel Dekker (1973).
3. L.G. Boxall, H.L. Jones and R.A. Osteryoung, "Solvent Equilibria in $\text{AlCl}_3\text{-NaCl}$ Melts," *J. Electrochem. Soc.*, 120 (2), 223 (1973).
4. H. Lloyd Jones, L.G. Boxall and R.A. Osteryoung, "Organic Electrode Reactions in Fused AlCl_3 Containing Solvents," *J. Electroanal. Chem.*, 38, 476 (1972).
5. L.G. Boxall, H.L. Jones and R.A. Osteryoung, "Electrochemical Studies on Ag, Fe and Cu Species in $\text{AlCl}_3\text{-NaCl}$ Melts," *J. Electroanal. Chem.*, 121, 212 (1974).
6. H. Lloyd Jones and R.A. Osteryoung, "Electrode Reactions of Aromatic Amines in Solvents Containing Fused AlCl_3 , II.", *J. Electroanal. Chem.*, 49, 281 (1974).
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Meeting Presentation and Seminars--Related to Grant Activity
(*Invited Presentations)

*R.A. Osteryoung, "Computerized Electrochemical Experimentation," Dept. of Chemistry Colloquia, Pennsylvania State University, University Park, PA, May 27, 1971.

*L.G. Boxall, H.L. Jones and R.A. Osteryoung, "Electrochemical Studies in Aluminum Chloride Melts", N.W. Regional ACS Meeting, Bozeman, Montana, June, 1971.

*R.A. Osteryoung, "Application of a Computer-Based Pulse Polarographic System in Molten Salt Studies", Gordon Research Conference on Molten Salts, Kimball Union Academy, Meriden, N.H., August, 1971.

*R.A. Osteryoung, "Use of a Mini-Computer in Electrochemical Studies", Symposium on Mini-Computers in the Research & Teaching Laboratory, American Chemical Society Meeting, Washington, D.C., September, 1971.

*R.A. Osteryoung, "Chemistry and Electrochemistry in Fused Salts," Baylor University, May 8, 1972.

*R.A. Osteryoung, "Computer Controlled Electrochemical Experimentation", Texas A & M (College Station, Texas ACS Section), May 11, 1972.

H.L. Jones, L.G. Boxall and R.A. Osteryoung, "Organic Electrochemistry in Aluminum Halide Melts", Rocky Mountain Regional ACS Meeting, Ft. Collins, CO, June 1972.

*R.A. Osteryoung, H.L. Jones and L.G. Boxall, "Electrochemical Studies in Molten Chloroaluminates", Symposium on Fused Salt Technology, Electrochemical Society Meeting, Chicago, May 8-13, 1973.

*R.A. Osteryoung, R.H. Abel, L.G. Boxall and B.H. Vassos, "An Introduction to the On-Line Use of Digital Computers in Electrochemistry", Plenary Lecture at Symposium on Electrochemical Measurements by Digital Computer, Electrochemical Society Meeting, Chicago, May 8-13, 1973.

D.E. Bartak and R.A. Osteryoung, "Oxidation of Tetramethylbenzidine in Chloroaluminate Melts", Electrochemical Society, San Francisco, CA, May, 1974.

*R.A. Osteryoung, "Chemistry in Aluminum Chloride Melts", Fifth International Conference in Non-Aqueous Solutions, International Union of Pure and Applied Chemistry, Vienna, July 10-12, 1974.

*R.A. Osteryoung, "Electrochemical Studies in Fused Salts", First Latin American Electrochemistry and Corrosion Meeting (ABRACO), Rio de Janeiro, Brazil, Oct. 21-25, 1974.

*R.A. Osteryoung, "Some Applications of Pulse Techniques to Analytical Chemistry and Electrochemistry," University of Brussels, Brussels, Belgium, March 17, 1975.

V.R. Koch, L.L. Miller and R.A. Osteryoung, "Electroinitiated Friedel-Crafts Transalkylation in a Room Temperature Molten Salt Medium," Mile High Electrochemistry Symposium, Colorado Electrochemical Society Section, Fort Collins, CO, May 3, 1975.

K.A. Paulsen and R.A. Osteryoung, "Electrochemical Studies of Sulfur in Molten Sodium Tetrachloroaluminate," Fall Meeting, American Chemical Society, Chicago, Illinois, August 1975.

*R.A. Osteryoung, "Chemistry and Electrochemistry in Aluminum Chloride Molten Salt Systems," International Symposium on Molten Salts, Spring Meeting, The Electrochemical Society, Washington, D.C., May 2-7, 1976.

*R.A. Osteryoung, "Electrochemical Studies in Molten Sodium Chloride-Aluminum Chloride," Colorado College, Colorado Springs, Colorado, December 4, 1975.

*R.A. Osteryoung, "Electrochemical Studies in Molten Chloroaluminates," Gould, Inc., Rolling Meadows, Illinois, March 4, 1976.

*R.A. Osteryoung, "Chemical and Electrochemical Studies in Molten Chloroaluminate Solvents," Dept. of Chemistry Colloquium, Purdue University, W. Lafayette, Indiana, March 23, 1976.

*V.R. Koch, L.L. Miller and R.A. Osteryoung, "Electroinitiated Friedel-Crafts Transalkylations in a Room Temperature Molten Salt Medium," Symposium on Electroorganic Oxidations, Electrochemical Society Meeting, Washington, D.C., May 2-7, 1976.

H. Chum, D. Koran and R.A. Osteryoung, "Studies in Room Temperature Molten Salt Systems," Mile High Electrochemistry Second Annual Symposium, Rocky Mountain Section, Electrochemical Society Meeting, Fort Collins, CO, May 15, 1976.

J. Robinson and R.A. Osteryoung, "The Electrochemical Behavior of Selenium in NaCl-AlCl₄ Melts," American Chemical Society Meeting, New Orleans, LA, March 20-25, 1977.

*K. Paulsen and R.A. Osteryoung, "Electrochemical Studies in Molten Chloroaluminates: Sulfur and Sulfides," Rocky Mountain Regional Meeting, American Chemical Society, Laramie, Wyoming, June 17-19, 1976.

*H.L. Jones, K. Paulsen, D. Bartak, J. Robinson and R.A. Osteryoung, "Acid-Base Dependent Electrochemistry in Molten Sodium Tetrachloroaluminate Solvents," Symposium on Spectroscopic and Electrochemical Characterization of Solute Species in Non-Aqueous Solvents, American Chemical Society Meeting, San Francisco, CA, August 29-September 3, 1976.

Helena Li Chum, D. Koran and R.A. Osteryoung, "Room Temperature Molten Salts and Its Mixtures with Benzene - New Solvents for Spectroscopic and Electrochemical Studies," Physical Chemistry Division, American Chemical Society Meeting, San Francisco, CA, August 29-September 3, 1976.

*R.A. Osteryoung, "Chemistry & Electrochemistry in Molten Chloroaluminates (Including Some Possible Applications to Sulfide Ores)," Environmental Impact Center, Newton, MA, October 27, 1976.

*R.A. Osteryoung, "Chemical and Electrochemical Studies in Molten Chloroaluminates," Department of Chemistry, University of Chicago, Chicago, IL, February 7, 1977.

*R.A. Osteryoung, "Electrochemical Studies in Molten Chloroaluminates," 4th Biennial Air Force Electrochemistry Conference, F.J. Seiler Research Laboratory, U.S. Air Force Academy, CO, April 28-29, 1977.

*R.A. Osteryoung, "Recent Trends in Electrochemical Research," Energy Research and Development Administration, Materials Science Workshop in "Electrochemistry and Thermodynamics," Argonne National Laboratory, Lamont, IL, May 19-20, 1977.

*R.A. Osteryoung, "Acid-Base Dependent Electrochemistry in Aluminum Halide Molten Salts," Gordon Research Conference on Molten Salts and Metals, Tilton, N.H., July 24-29, 1977.

*R.A. Osteryoung, "Chemistry and Electrochemistry in Molten Chloroaluminates," Georgia Institute of Technology, Atlanta, GA, October 12, 1977.

*R.A. Osteryoung, "Chemistry and Electrochemistry in Molten Chloroaluminates," Georgetown University, Washington, D.C., February 9, 1978.

J. Robinson and R.A. Osteryoung, "The Electrochemistry of Selenium in Molten Sodium Tetrachloroaluminates," 3rd Annual Mile High Symposium on Electrochemistry, Rocky Mountain Section of the Electrochemical Society, Fort Collins, CO, May 7, 1977.

R.A. Osteryoung and B. Gilbert, "Electrochemistry of Nickel in Molten Sodium Tetrachloroaluminates," National American Chemical Society Meeting, Anaheim, CA, March 12-17, 1978.

*R.A. Osteryoung, "Chemistry and Electrochemistry in Molten Chloroaluminates," Wichita State University, Wichita, KA (April, 1978).

*R.A. Osteryoung, "Electrochemistry in Molten Chloroaluminates," Naval Surface Weapons Center, White Oak, Maryland (May, 1978).

*R.A. Osteryoung, "Acid Base Dependent Electrochemistry in Chloroaluminate Melts," Conference on Highly Concentrated Aqueous Solutions and Molten Salts, Oxford University, Oxford, England (July 5-7, 1978).

*R.A. Osteryoung, "Acid Base Dependent Chemistry and Electrochemistry in Chloroaluminate Melts," The University of Southampton, Southampton, England (July 10, 1978).

*R.A. Osteryoung, R.J. Gale, J. Robinson, R. Bugle and B. Gilbert, "Electrochemical Studies in a Room Temperature Molten Salt," Second International Symposium on Molten Salts, The Electrochemical Society, Pittsburgh, Pennsylvania (October 15-20, 1978).

*R.A. Osteryoung, "Acid-Base Dependent Chemistry and Electrochemistry in Molten Chloroaluminates," Gould, Inc., Rolling Meadows, IL, November 16, 1978.

*R.A. Osteryoung, "Acid-Base Dependent Chemistry and Electrochemistry in Molten Chloroaluminates," Colorado Section, American Chemical Society, University of Colorado, December 12, 1978 (Colorado Section Award Talk).

*R.A. Osteryoung, "Studies in Molten Chloroaluminates," Oak Ridge National Laboratory, Oak Ridge, TN, Feb. 2, 1979.

*R.A. Osteryoung, J. Robinson and R.J. Gale, "Oxidation of Aromatic Hydrocarbons in a Room Temperature Molten Salt," Symposium on Electrochemistry and Spectroscopy in Melts, American Chemical Society/Chemical Society of Japan Congress, Honolulu, Hawaii, April 1-6, 1979.

*R.J. Gale, A.J. Nozik and R.A. Osteryoung, "Electrochemical Characterization of the Semiconductor TiO_2 -Room Temperature Molten Salt Interface", Rocky Mt. Regional Electrochemical Society Meeting, Ft. Collins, CO (June, 1979).